there appear terms representing screening on a static picture of the atom. These were omitted since their effects can be estimated by other methods. Otherwise the calculation is similar to that for the dipole effect and Equations (15) and (15′) obtain.

The authors would like to thank Professor G. Breit for suggesting the reaction channel method and the separation of the products of Coulomb functions into high and low frequency parts, and for stimulating discussion.

* This research was supported by the United States Air Force under Contract No. AF 18 (600)-771 monitored by the AF Office of Scientific Research of the Air Research and Development Command.

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[5] The authors would like to thank Professor G. Breit for suggesting the coordinate system used in the calculation of Coulomb Excitation effects.

[6] Breit, G., E. U. Condon, and R. D. Present, *Phys. Rev.*, **50**, 825 (1936).

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*A SURVEY OF OUR PRESENT SOURCES OF INFORMATION ON THE CONVERSION CONSTANT, $\Lambda(=\lambda_g/\lambda_s)$ AND THE ABSOLUTE WAVELENGTHS OF X-RAY EMISSION LINES**

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Communicated May 4, 1959

Origin of the "X-Unit" and the Scale of X-Ray Wavelengths.—The wavelengths of X-ray emission lines measured relative to each other by the high precision methods of crystal diffraction are mostly known with a precision of 1 part in 10^4 to 10^5. By refined and very careful measurements with the 2-crystal spectrometer, an imprecision approaching and in some cases perhaps even smaller than a part in a million can be obtained. This precision exploration and tabulation of the X-ray spectrum was first brought to high perfection by Manne Siegbahn[1] and his school. Later, with such further improvements as the two-crystal spectrometer and the curved crystal spectrometer, it was carried even further by many others.[2–5] About 3000 of these precision wavelength measurements have been tabulated,[4] and they constitute a very reproducible and well-defined set of fixed points in the natural scale of lengths in the range between about 10^{-9} and 4×10^{-6} cm. The method employed for measuring them does not, however, yield their values directly in our cgs system of units since the interplanar grating spacings of the atomic planes in crystals are the yardsticks used. To express these wavelengths in centimeters or Angstrom units the method first adopted was that of Sir William Bragg,[6] whose reasoning was as follows.

In the simple case of the cubic structure of a rock-salt crystal, see Figure 1, each atom (sodium or chlorine) is associated with a volume, d^3, whose weight is ρd^3, where $\rho = 2.17$ gm cm^{-3} is the macroscopically measured crystal density. Now 1

mole, that is to say 23.05 + 35.45 = 58.50 gm of rock salt,† will contain $2N$ molecules, where N is the Avogadro number, so that the mean weight per atom will be $58.50/(2N)$ gm. Equating this to ρd^3, the mean weight of crystal associated with each atom, we have

$$\rho d^3 = 58.50/(2N) \tag{1}$$

$$d = (58.50)^{1/3}/(2N\rho)^{1/3} = 2.814 \times 10^{-8} \text{ cm} \tag{2}$$

provided we use for N the value Millikan obtained as the quotient of the Faraday by his oil-drop value of $e = 4.774 \times 10^{-10}$ esu. Unfortunately this latter value was about 0.6 per cent too low because in computing e from his oil-drop observations Millikan had used an erroneous value of η, the viscosity of air, as determined by Harrington. About a decade elapsed, however, before these errors were revealed.

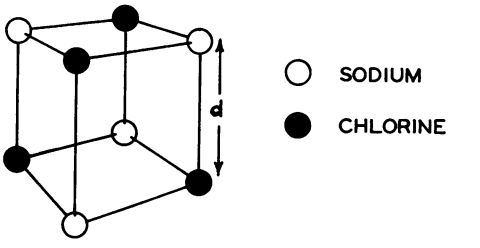

FIG. 1.—Cubic structure of a rock-salt crystal, illustrating Sir William Bragg's original method of computing the grating space, d, given the Avogadro number, the crystal density, and its molecular weight.

The structure of rock salt is less perfect and less reproducible from sample to sample than certain other crystals; calcite, for example. In 1925 Compton, Beets, and DeFoe[7] made very careful measurements on the latter rhombohedral crystal to determine its density and the angles between its cleavage planes. The latter goniometric measurement permits calculation of the volume of a calcite rhombohedron having unit separation between its three pairs of parallel faces. They found for this volume, $V = 1.09630 \pm 0.00007$. (In later work J. A. Bearden[38] obtained a slightly different numerical value.) As a final result of their calculation, whose principle is the same as that just described for rock salt, they obtained for the true grating space a value which M. Siegbahn *adopted* as the basis for calculating X-ray wavelengths. This calculated grating space was, however, erroneous chiefly because of the error in Harrington's value of η with its consequent effects on e, and thence on the value of $N = F/e$ which Compton, Beets, and DeFoe had used.

In view of these errors it is best to regard Siegbahn's system of wavelengths as a purely arbitrary, albeit highly reproducible system, and indeed Siegbahn *very wisely* chose to call the unit length in that system by a distinctive name, the x-unit, for although he had certainly intended to make the x-unit as nearly as possible equal to a milliangstrom, it seems highly likely that from the beginning he felt more insecurity about its absolute value than was comfortable in view of the high precision with which X-ray wavelengths could be measured relative to each other by means of crystals. For many years no distinction between x-units and milliangstrom units was suspected. The terms were used interchangeably. Now that the discrepancy between them is well established it is customary merely *to define the x-unit* as Siegbahn and the rest of us have come to do, by the statement that the "effective"‡ grating space of the calcite cleavage planes at 18°C for first order Bragg reflection is

$$d_{18}'' = 3029.040 \text{ x-units} \quad (3)$$

The author believes, for reasons to be discussed in this paper, that it would be still better to define the x-unit in terms of at least one or perhaps more carefully chosen standard X-ray emission lines. This point will be discussed in due course.

$\Lambda(= \lambda_g/\lambda_s)$ *the Ratio of the X-Unit to the Milliangstrom Unit.*—The discrepancy between Siegbahn's x-unit and the milliangstrom unit first began to be manifest when the wavelengths of certain soft X-ray lines which had been measured in x-units by the methods of crystal diffraction were also precisely measured with artificially ruled gratings whose grating constants had been calibrated using known or calculable optical wavelengths. Apparently the first to note the discrepancy was Erik Bäcklin in his thesis dissertation at Uppsala (1928).

Because of the deservedly great prestige of R. A. Millikan and the rather obscure nature of the true source of error, more than a decade elapsed before there was general acceptance that Millikan's value of e was seriously erroneous. During this period there was much discussion of the "discrepancy" between the "oil-drop" and the "X-ray" values of e. Several rather far-fetched proposals to explain this discrepancy were made by proponents of the Millikan value before the error in η, the viscosity of air, was definitely established as the chief source of the trouble: (1) It was proposed that a mosaic structure or that impurities in the crystals might be responsible. (2) It was suggested that the laws of optics might not be applicable to the diffraction of X-rays from ruled gratings at grazing incidence; a careful analysis by C. Eckart refuted this. (3) The grating constant measured with X-rays might not be the same as the grating constant throughout the bulk of the crystal lattice. This third criticism was the most tenacious and the most difficult to refute. The Bragg reflection from atomic planes parallel and very close to a boundary surface had always been used in precision determinations, and since the surface is admittedly a highly specialized locality, the atomic structure and hence the grating constant might conceivably have a special value there. (An analogy might be made with surface tension in liquids.) The macroscopic density measurements of a crystal used by Sir William Bragg, A. H. Compton, or M. Siegbahn in their method of computing the grating constant, on the other hand, clearly must yield the average grating constant over the entire sample of crystal. The plausibility of this criticism and also that of the first one was greatly weakened by showing[8] that the measured densities and X-ray values of grating constants combined with molecular weights gave, for many different kinds of crystals of the perfect type, mutually consistent values of the Avogadro number, N. (Reversing the Bragg method of calculating crystal grating constants, if we know from X-ray measurements the grating constant, d, of a crystal, its density, ρ, the molecular weight, M_μ, of its unit cell, and the dimensionless geometrical shape factor, ϕ, the volume of a unit cell whose grating constant, d, is unity, we can calculate Avogadro's number, N, from $N = M_\mu/(\rho\phi d^3)$. The third criticism persisted for a time nonetheless because of a suggestion by F. Zwicky that a superlattice structure, consisting of periodic local deviations of the lattice from the average grating spacing, might be a general property of all crystal lattices because of some very fundamental far-reaching and general "cooperative" effect extending over wide domains. Zwicky suggested that the boundary surface of a crystal might, by some considerations of

minimum energy, be invariably the site of one of these abnormal grating constant regions. The third criticism was removed entirely, however, by two methods: (*a*) X-rays were reflected from crystals of the perfect type such as calcite using *internal* atomic planes for this purpose and the internal grating constant was shown to be the same as at the surface;[9, 10] (*b*) Crystals such as calcite and quartz were powdered so finely that the penetration of X-rays through each grain was complete and not appreciably limited by "extinction." The grating constant for the powder was then measured with high precision using a Seeman-Bohlin spectrograph, and the density of the identical sample of powdered crystal was measured with a pycnometer. No significant deviation was observed in the inferred value of N from that obtained with macroscopic crystals used in Bragg surface reflection.[9, 11] Several experimeters have repeated the oil-drop experiment and also the determination of the viscosity of air and it is now quite clearly established that no real discrepancy exists between the X-ray and oil-drop values of e.

Save for the case of extremely long X-ray wavelengths the great bulk of the ruled grating measurements of X-ray lines have been made using plane gratings by the method of grazing incidence. Compton and Doan[12] and shortly afterward Thibaud[13] were the first to use this method. In grazing incidence far greater dispersion is obtainable with a grating of a specified number of rulings per unit distance than in the more familiar case of normal incidence.

A condition for sufficient intensity in the diffracted spectrum is that the angle of grazing incidence shall be less than the critical angle for total reflection. It should be recalled that the refractive indices of X-rays are in most cases less than unity. Total reflection occurs therefore in the less dense medium. Rather coarse gratings with a fairly large ratio of flat intervening space to the width of the ruled lines are usually used and methods of ruling which are likely to produce a projection of the ruled material above the flat intervening surfaces are to be avoided.

The geometry controlling the path difference, $PB\text{-}AR = a[\cos\theta - \cos(\theta + \alpha)]$, is shown in Figure 2. It must be recalled that for X-rays no lenses are available to

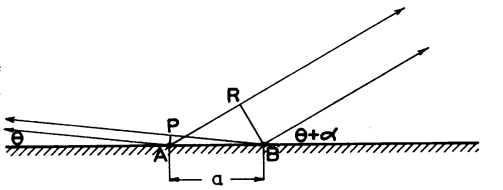

FIG. 2.—Illustrating the geometry of the path difference when ruled gratings are used in grazing incidence to measure X-ray wavelengths; a is the grating spacing.

render a divergent beam parallel or to focus a parallel beam to a point, as in the case of ordinary optical light. Setting the path difference equal to a whole number of wavelengths, $n\lambda$, we have

$$n\lambda = a[\cos\theta - \cos(\theta + \alpha)]. \tag{4}$$

In the simplest of all cases when θ can be regarded as negligible we have

$$n\lambda = a(1 - \cos\alpha) \cong a\alpha^{2}/_{2}. \tag{5}$$

The dispersion for grazing incidence, $(d\alpha/d\lambda)_g$, is

$$(d\alpha/d\lambda)_g = \sqrt{n/(2a\lambda)}. \tag{6}$$

This is to be compared with the dispersion for normal incidence, $(d\alpha/d\lambda)_n$, which is

$$(d\alpha/d\lambda)_n \cong n/a, \text{ for small } \alpha. \quad (7)$$

The chief precision wavelength measurements of X-ray characteristic spectral lines by diffraction on ruled gratings to date have been made by four authors, J. A. Bearden,[14] E. Bäcklin,[15] and M. Söderman,[16] and F. Tyrén,[17] between 1931 and 1938. The softer X-ray lines CuKα, β, AlKα were chosen for study. The results are best expressed in terms of the conversion factor $\Lambda = \lambda_g/\lambda_s$ implied by the measurements and these will be found in Table 1.

TABLE 1

COMPARISON OF GRATING AND SIEGBAHN WAVELENGTHS OF X-RAYS (1945)

Author	X-Ray Line	$(\Lambda - 1) \times 10^6$ (The Probable Error Is Based on Accidental Errors Only)	Adopted Probable Error
Bearden*	CuK$\alpha_{1,2}$	1980 ± 31	±52
Bearden*	CuK$\beta_{1,3}$	2079 ± 28	±50
Bearden*	CrK$\alpha_{1,2}$	2036 ± 21	±48
Bearden*	CrK$\beta_{1,3}$	2017 ± 28	±48
Söderman†	AlK$\alpha_{1,2}$	2070 ± 37	±84
Bäcklin‡	AlK$\alpha_{1,2}$	2000 ± 14	±60
Bearden§	CuK$\alpha_{1,2}$	2087 ± 55	±130
Tyrén‖	AlK$\alpha_{1,2}$	2024 ± 5	±48
	Adopted average	2030 ± 20	

* Bearden, J. A., *Phys. Rev.*, **37**, 1210 (1931).
† Söderman, M., *Nature*, **135**, 67 (1935); Dissertation, Uppsala, 1934.
‡ Bäcklin, E., *Z. Physik*, **93**, 450 (1935).
§ Bearden, J. A., *Phys. Rev.*, **48**, 385 (1935).
‖ Tyrén, F., *Z. Physik*, **109**, 722 (1938).

The measurements of Λ in Sweden were chiefly done using concave grating vacuum spectrographs with grazing incidence angles on the grating of order 1°. Perhaps the best and most carefully performed of these were the measurements of F. Tyrén in his dissertation.[17] His method consisted in recording on one and the same Schumann plate, bent to conform to the Rowland circle of his instrument, two sets of lines: (1) Calibration lines consisting of Lyman Series spark lines from one-electron (hydrogenic) ionized atoms, O^{VIII}, N^{VII}, C^{VI}, B^{V}, and Be^{IV} and (2) soft X-ray lines which had already been measured using crystals and were therefore known on the "crystal scale" in x-units and were to be determined by interpolation from the calibration lines on the nonlinear wavelength scale of the plates. Tyrén computed the wavelengths of the calibrating spark lines in angstrom units using the very accurately known value of the Rydberg and theoretical spectroscopic formulas based on the Bohr-Sommerfeld-Dirac theory for the hydrogen-like atom. At the time Tyrén wrote his thesis the Bohr-Sommerfeld-Dirac theory was considered absolutely correct, but a few years later the advent of the Lamb shift and its explanation in terms of modern quantum-electrodynamics called for a correction to the Bohr-Sommerfeld-Dirac theory, the magnitude of which is different and far from negligible for each of Tyrén's calibration lines. Although the need for this correction to Tyrén's result was (by their own later admission) recognized by some of the Swedish school of spectroscopists as soon as Lamb's discovery was published, no attention was publicly called to it and it went completely unnoticed until as late as 1956 when the present writer and E. R. Cohen published a note[18] about it. Table 2 shows these Lamb shift corrections calling for increases in the calibration

TABLE 2

RELATIVE INCREASES REQUIRED TO CORRECT TYRÉN'S REFERENCE WAVELENGTHS FOR THE LAMB SHIFT

Tyrén's calibration wavelengths, Lyman series lines of O^{VIII}, N^{VII}, C^{VI}, B^{V}, Be^{IV} were calculated using a formula in conformity with the Sommerfeld-Dirac theory of the one-electron atom. The Lamb shift corrections, $\Delta E/E$, to this formula in ppm are:

n		O^{VIII}, ppm	N^{VII}, ppm	C^{VI}, ppm	B^{V}, ppm	Be^{IV}, ppm
1	Lyman alpha	98.5	81.5	64.5	49.0	34.5
2	Lyman beta	84.0	69.0	54.7	41.0	29.0
3	Lyman gamma	79 0	65 5	52 0	39 1	27.5
4	Lyman delta	77.5	63.5	50.4	38.3	26.8

Note: For $np - 1s$ transitions $\Delta E/E = [8n^2/[3\pi(n^2 - 1)]](7.723 - 2 \ln Z - 0.0439/n^3)$.

wavelengths which vary from 98.5 parts per million (ppm) to 26.8 ppm. Unfortunately Tyrén's thesis does not specify just how the calibration lines were associated with the X-ray lines and since both sets of lines were recorded in many different orders (up to the 13th in the case of some X-ray lines) one cannot conclude that X-ray lines and spark lines most closely adjacent in wavelength were necessarily those associated for the purpose of calibration. It is to be hoped that Tyrén's original notes and calculations and also his original plates can be secured and corrected for the Lamb shift but no such correction has as yet been made. Tyren's result, $\Lambda = 1.00199$ (which he stated without giving any estimated standard deviation), must certainly therefore be increased by some amount between 26.8 and 98.5 ppm. A rough estimate by E. R. Cohen based on the assumption that those calibration spark lines and X-ray lines most nearly adjacent in wavelength were associated, yields a corrected average value for Tyrén's determination of $\Lambda = 1.002026 \pm 0.000016$. Little significance can be attached to this, however, save to show that the correction certainly seems to promise better consistency between Tyrén's results and those obtained chiefly by J. A. Bearden in the United States using plane ruled gratings.

Importance of the Conversion Constant, Λ, in the Determination of the Entire System of Constants and Conversion Factors of Physics and Chemistry.—The importance of the conversion constant, Λ, in contributing to our knowledge of *all of the fundamental constants of atomic physics*, though little realized, can hardly be overstated since it is the bridge between our tangible macroscopic scale of length magnitudes and the scale of atomic length magnitudes. Because of the many intricate relations which now link all of the fundamental atomic constants of Physics and Chemistry a revision in the directly measured value of Λ would have extremely for reaching effects on our present state of knowledge of all of the fundamental constants. For example in our 1955 least squares evaluation of the constants,[19] far each part per million change in the directly measured input value of Λ, the resulting change in parts per million which eight important output constants would sustain is shown in Table 3.

It must not be supposed that the differential coefficients whose numerical values are given in Table 3 are constants of nature. They are bound to change with every new least-squares adjustment to obtain "best" values because they depend on which functions of the atomic constants were those whose measured values constituted the input data of the particular adjustment and also on the precision with which those measurements were made. Both of these things are altered from their

previous state at every epoch when a new adjustment is effected, because of the progress of measuring techniques, and indeed a new adjustment would not be warranted unless such changes had occurred. However, it is hopeless to anticipate a time when such interrelationships will vanish.

TABLE 3

CHANGES, IN PPM, SUSTAINED BY EIGHT IMPORTANT OUTPUT VALUES OF ATOMIC CONSTANTS AS A RESULT OF A CHANGE OF 1 PPM IN THE DIRECTLY MEASURED INPUT VALUE OF Λ IN THE COHEN, DuMOND, LAYTON, AND ROLLETT LEAST SQUARES ADJUSTMENT OF 1955

e	0.14
m	0.22
h	0.26
α	0.02
Λ	0.21
N	−0.21
F	−0.07
$hc^2/(e\Lambda)$*	−0.08

* This is the voltage-wavelength conversion factor whose adjusted value as an output result of the 1955 adjustment, was 12372.44 ± 0.16 kv X-units. Dividing this number by any wavelength expressed in X-units gives the corresponding quantum energy in electron-kilovolts.

Proposal to Express the International Crystallographic Wavelength Tables in Milliangstrom Units; Advantages and Disadvantages.—The present survey of the state of our knowledge of Λ is of considerable current interest and was undertaken chiefly because of a proposal now very seriously being considered on the part of crystallographers, particularly for the preparation of the new International Tables of Crystallography, to tabulate all the wavelengths of the standard X-ray emission lines in angstrom units rather than as heretofore in x-units on the crystal scale. Those who favor this step at the present time do so because they believe it will lead to simplification and will avoid a great deal of confusion now assertedly resulting from ignorance on the part of some crystallographers of the distinction between the x-unit and the milliangstrom unit. The author of this paper would only agree with this point of view if it were possible to establish beyond all reasonable doubt the conversion from the x-units of the crystal or Siegbahn scale, in terms of which the X-ray lines were measured, to milliangstrom units with the same or preferably with better precision than the precision with which the X-ray line measurements were made on the x-unit scale. For, if this is not possible, then either (1) the tabulation of all the X-ray reference line wavelengths in terms of numbers labeled angstrom units must be seriously down-graded to a precision far poorer than the best available precision with which X-ray wavelengths are known relative to each other to allow for the imprecision in our knowledge of the single conversion constant afflicting all of the data, or (2) some conventional value of the conversion constant must be adopted by general consent to which a fictitiously high precision is assigned. But in this last case we shall not in reality be telling the truth if we label the numerical values so computed as values expressed in milliangstrom units for we shall be doing once more (on a different level of precision, it is true) exactly the same thing which was done when the x-unit was established with the aim of making it equal to a milliangstrom. Hence, sooner or later, we shall surely discover that instead of simplifying the situation and avoiding confusion, we have increased the confusion by printing tables which are expressed in terms of a unit which is neither exactly a milliangstrom nor an x-unit and which for definiteness will thenceforth

have to be given a name. Such a unit might well deserve to be named "The Folly of the Crystallographic Congress of 1959."

The temptation to circumvent a real difficulty of physical measurement by introducing a conventionally defined conversion constant, so prevalent at International Congresses, is becoming increasingly important to resist because of the ever increasing tightness with which all the different quantities of Physics and Chemistry are interrelated. The specialist in a given field is not likely to be as aware of the intricate tightness of these interrelationships as are those, like Dr. Cohen and myself, who have concerned themselves for a long period of time with efforts to distill from the entire mass of information in both Physics and Chemistry the best values of all the constants of those related disciplines. Such a task can no longer be tackled piecemeal. The two disciplines cannot be treated separately. The entire system is like an immense cobweb. You pull on any of the filaments and the whole pattern changes to some extent. Starting from the present wealth of observational data there are no longer any well marked single routes by which to arrive at values of a specified constant or conversion factor. Each desired result can be arrived at by a multiplicity of different single-track (just-determinate) routes no one of which is by any criterion so greatly to be preferred to all others as to indicate it indubitably for acceptance. We have no escape in this situation save through very comprehensive least-squares analyses very carefully combed in an effort to detect and cast out systematically erroneous data. Unless the practitioners of each specialized field, crystallography, thermodynamics, X-rays, nuclear physics or what you wish, realize that they can no longer regard their particular discipline as an area isolated from the rest of Physics and Chemistry, the beautiful edifice which together the builders of these two divisions of science have constructed will become a Tower of Babel.

How Accurately Can X-Ray Wavelengths be Expressed in Millionsgstrom Units by Direct Determinations of Λ?—It is for the foregoing reason that the author of this paper deems it timely and desirable to examine with some care just how much we presently know, from all sources of information, both direct and indirect, about this conversion constant, Λ ($= \lambda_g/\lambda_s$).

Table 1 above, prepared by R. T. Birge[20] in 1945, shows the directly measured data on Λ from all sources then available, both the flat grating work of Bearden, in which no calculated calibration wavelengths were needed because the incidence and reflection angles were directly measured, and the Swedish concave grating work. Tyrén's 1940 dissertation results, which were afflicted with the systematic error from the Lamb shift as above explained, are not included in this tabulation but it seems likely that the 1938 work of Tyrén which is shown in the last item suffers from the same error; but to what extent we do not know. This single item, if corrected, would probably have little effect on Birge's final weighted average which was:

$$\Lambda = 1.002030 \pm 0.000020 \text{ (Birge, 1945)} \quad (8)$$

This value agreed (save for a larger assigned error measure) with a weighted average obtained earlier by J. A. Bearden.[21] The Birge 1945 value was accepted and used until in 1947 Sir Lawrence Bragg issued an ex-cathedra statement which appeared in several journals widely read by crystallographers in England and the

United States[22] to the effect that "after consultation with Siegbahn, Warren, and Lipson, and with due consideration given to the above data listed by Birge," he recommended for general adoption the value

$$\Lambda = 1.002020 \pm 0.000030 \text{ (Bragg edict of 1947).} \quad (9)$$

No statement of any basis in new physical measurements was given to justify this edict. The author of this paper could obtain no clear explanation from Sir Lawrence Bragg or for a long period from any one else as to just how this value had been arrived at and in particular why Birge's 1945 average had been deliberately altered, until in 1956 he happened to broach the subject with R. T. Birge himself, who it seems was much more involved in the controversy and compromise than the innocuous wording of the edict first led the present writer to suppose. It appears that the chief argument for a downward revision in 1947 of Birge's average value was due to M. Siegbahn who urged it because of the result of Tyrén's dissertation, Uppsala 1940,

$$\Lambda = 1.00199 \text{ (Tyrén, Dissertation 1940)} \quad (10)$$

to which no error estimate had been attached by its author. M. Siegbahn at the time was, however, so impressed with the excellence of this work (and indeed it was beautifully executed, though the details of the interpolation were not as clearly revealed in the dissertation as one could wish) that he agitated strongly for a revision downward of Birge's value. Siegbahn had at the time, of course, no way of foreseeing the discovery of the Lamb shift three years later. Birge, on the other hand, chiefly because of the convincing nature of Bearden's results with plane gratings, refused to consent to lowering of his weighted average of 1945 by more than one unit in the fifth decimal place and would accept that only if a correspondingly greater spread were assigned in the error measure. Actually, if, as, and when Tyrén's observations and calculations can be corrected for the Lamb shift, it now appears not unlikely that the apparent discrepancy between Tyrén's 1940 result above and Birge's weighted average of 1945 will be essentially wiped out. The world therefore probably owes Birge a debt of gratitude for his refusal to modify Λ more drastically. After a lengthy period of correspondence, in the full knowledge of a serious unexplained discrepancy and without any published explanation of the doubtful procedure, the value given in the Bragg edict of 1947 was recommended and promulgated. Such authoritarian practices (publishing a recommendation for adoption of an important conversion constant *with no detailed public statement of reasons or experimental bases*) is greatly to be deplored as completely contrary to the spirit of science![§]

It appears that though the Swedish school of precision X-ray spectroscopists made no effort to warn the rest of the world of a systematic error in the results of Tyrén on Λ after the Lamb shift had become an established fact, they did feel sufficiently insecure about Tyrén's $\Lambda = 1.00199$ to continue energetically a program directed at bettering this determination and several pieces of work about which little has been published have been performed. For example, an unpublished recent piece of work of Björkman at Uppsala following the same method as Tyrén has yielded a surprisingly high value

$$\Lambda = 1.00216 \pm 0.00004 \text{ (Björkman unpublished)} \quad (11)$$

140 ppm higher than the Bragg edict of 1947! Björkman's manuscript does not make it clear whether the Lamb shift was taken into account in his calculations.

If we examine Birge's Table 1 we see that the error estimate for the weighted average calculated by the methods of statistics (valid when the errors are purely random) arrives at a "probable error" of only 20 ppm. Actually the eight individual values averaged wander all the way from 1.001980 to 1.002087, a spread of 107 ppm and one should therefore not be too surprised or disappointed to discover later that systematic errors may well have been present which distorted the average considerably more than the statistically computed error.

Because of the great importance of this constant, Λ, and because the uncertainties here discussed really throw this question wide open once more, redeterminations of its value are now being undertaken in two places and it would be highly desirable if similar projects could be started elsewhere, preferably in publicly supported government standards laboratories where the expense of a long program of extremely careful work on such a determination can be more logically justified and supported. One of these two presently going programs on Λ is now in progress by Professor H. A. Kirkpatrick, with the collaboration of the present author, utilizing the method of Tyrén, with a concave grating of 42 foot radius of curvature in a vacuum spectrometer, the lines being recorded on Schumann plates. Professor Kirkpatrick is doing this work at the present moment at the University of Wisconsin as a guest in the laboratory of Professor Julian Mack to whom we are deeply grateful for the use of his vacuum spectrometer. The other program, I am told, is being pursued by Professor J. A. Bearden and his son at Johns Hopkins University utilizing plane gratings, in vacuum, the X-rays incident on the grating being first monochromatized by crystal diffraction. At the date of writing no definite results are available from either of these sources.

Indirect Information on the Value of Λ.—It is well worth while now to examine exhaustively just what indirect information on the value of Λ can be inferred from presently existing data of measurement. This can be conveniently done by considering all the input data, which were used in the 1955 adjustment of the fundamental constants of Cohen, DuMond, Layton, and Rollett[23] taking into account as far as possible such changes and corrections and new sources of information as have become available subsequently. The four primary unknowns, α, e, N, and Λ, whose least-squares adjusted best values were sought, together with the two groups of experimental data used in setting up the equations for the least-squares solution, are listed and defined in Table 4. In the first group, seven kinds of functions of the unknowns appear equated to their experimentally determined numerical values. Each equation is labeled with the experiment which leads to it. It must be understood, however, that in order to utilize the results of many of these experiments in equations involving only the four chosen unknowns, it has been necessary to combine with the experimentally measured quantity certain other extremely accurately known constants whose values are listed in the second group and whose accuracy so greatly surpasses the accuracy of the measurements listed in the first group that they do not contribute appreciably to the error of the result. Thus the "measured numerics" in the first group involve, for their computation, not only the experimental measurements listed under the heading "Description of Experiment," but also appropriately selected data from the second group requisite to give the

TABLE 4

RÉSUMÉ OF THE DATA CONSIDERED FOR THE 1955 LEAST SQUARES ADJUSTMENT OF COHEN, DuMOND LAYTON, AND ROLLETT

Four primary unknowns whose least squares adjusted values are sought:

- α ($= 2\pi e^2 h^{-1} c^{-1}$), Sommerfeld's fine structure constant.
- e, electronic charge (expressed in abs. esu).
- N, Avogadro number.
- Λ ($= \lambda_g/\lambda_s$), conversion factor from X-units (Siegbahn) to milliangstroms.

First Group (Least Squares Adjustment)
Seven Kinds of Experimental Data Bearing on Above Unknowns

Kind No.	Function	Measured Numeric	Estimated Precision (ppm)	Description of Experiment
1	Ne/c	= 9652.15	13	Iodine } Faraday by electrochemistry
	Ne/c	= 9651.29	20	Silver }
2	Λ	= 1.002020	30	X-ray lines measured with ruled gratings
3	$N\Lambda^3$	= 0.606179 × 10^{24}	38	Crystal densities and grating constants in X-units
4	$\alpha^2 c/e$	= 2.425517 × 10^{13}	23	Proton Gyrom. Ratio (Thomas, Driscoll, & Hipple)
5	$Ne^2/(\alpha^2 c^2)$	= 3.979879 × 10^{-10}	36	Bloch & Jeffries, "Inverse cyclotron" } Proton magn. moment in nuclear magnetons by measuring ω_c/ω_p
	$Ne^2/(\alpha^2 c^2)$	= 3.979423 × 10^{-10}	11	Sommer, Thomas & Hipple, "Omegatron"
	$Ne^2/(\alpha^2 c^2)$	= 3.979359 × 10^{-10}	14	Collington, Dellis, Sanders. & Turberfield
	$Ne^2/(\alpha^2 c^2)$	= 3.979444 × 10^{-10}	36	Kenneth R. Trigger's corr. to B & J
6	$\alpha^2 c$	= 1.596412 × 10^6	9	Microwave determination of fine structure splitting in deuterium — W. Lamb, Jr., and coworkers
7	ec/($\Lambda\alpha$)	= 1968.750	51	Felt, Harris, & DuMond } Short wavelength limit of continuous X-ray spectrum
	ec/($\Lambda\alpha$)	= 1968.911	40	Bearden, Johnson & Watts
	ec/($\Lambda\alpha$)	= 1968.869	83	Bearden & Schwarz

Second Group (Regarded as Fixed Constants)

H	= 1.008142 ± 0.000003 (Physical)	3	Atomic weights by method of nuclear reaction energies
H/M_p	= 1.00054461		
D	= 2.014735 ± 0.000006 (Physical)	3	
D/M_d	= 1.00027244		
R_∞	= 109737.309 ± 0.012 cm^{-1}	0.11	Spectroscopic determination of R_∞
μ_e/μ_p'	= 658.2288 ± 0.0004	0.6	Ratio electron magnetic moment to proton magnetic moment
μ_e/μ_0	= 1.00114536	<0.01	Ratio electron magnetic moment to Bohr magneton
c	= 299793.0 ± 0.3 km sec^{-1}	1	Velocity of light

numeric the significance indicated by the left-hand member of each equation.

The seven kinds of equations of Table 4, comprising a total of thirteen equations in four unknowns, are called "the primitive equations of observation." They constitute a highly overdetermined set whose mutual compatibility turned out to be considerably poorer than the *a priori* estimates of precision (shown in Table 4) would lead one to expect, thus casting strong suspicion that some members contain systematic errors.

Such a set is most conveniently adjusted and analyzed as to its compatibility after a "linearization" procedure as follows: A set of "origin values," α_0, e_0, N_0, and Λ_0, can easily be chosen for the unknowns which will lie within a few tens of parts per million of the least-squares adjusted values to be found. The origin values chosen were

$$\alpha_0 = 0.007297000 \tag{12}$$

$$e_0 = 4.802200 \times 10^{-10} \text{ esu} \tag{13}$$

$$N_0 = 0.6025000 \times 10^{24} \text{ mole}^{-1} \quad (14)$$

$$\Lambda_0 = 1.0020200 \quad (15)$$

We then re-express the unknowns and the constants of the thirteen equations of Table 4 in terms of new variables, $x_1 = 10^6 (\alpha - \alpha_0)/\alpha_0$; $x_2 = 10^5 (e - e_0)/e_0$, etc., and new constants $A = 10^5 (c - c_0)/c_0$ where c is the constant in the particular equation and c_0 the origin value that constant would have in order to be compatible with the four origin values selected for the unknowns, in other words we express the entire set in terms of small relative deviations in parts per hundred thousand from an arbitrary origin point in the space of the four unknowns, a point selected so as to lie close to the final solution. This is essentially the same as expressing the equations in terms of the logarithms of all the quantities and in this new convenient linearized form one obtains a set of linear equations of which we will only write out a few samples as illustrations:

	Weight	Description of Experimental Source
$x_2 + x_3 = 11.1$	0.58	(Iodine) Faraday by electro-chemistry
$x_4 = 0$	0.11	$\Lambda = 1.002020$, Bragg edict
$x_3 + 3x_4 = 3.5$	0.07	Crystal densities and grating constants in X-units
$3x_1 - x_2 = -2.3$	0.19	Thomas Driscoll & Hipple gyromagn. ratio of proton

These then are the overdetermined linear equations to which the well-known classical procedure of least squares is applied to determine a set of "adjusted values" for the unknowns. The measure of compatibility used is called χ^2 and is defined as the sum of the squares of the normalized residues of all the linearized equations. The residue of an equation is the amount by which it fails to balance when the least-squares adjusted values of the unknowns are substituted in it and the normalized residue is the actual residue divided by the *a priori* standard deviation attached to the numeric of that equation. χ^2 is in fact the minimum value of the quantity which it is the objective of the method of least squares to minimize. In the present instance χ^2 turned out to be 52.1 whereas its expected value (in the absence of systematic errors) should be 8. A search for suspiciously incompatible equations was then made by an elaborate digital computer program described in detail in the 1955 paper[23] and in this way six equations were spotted and, in the case of each, valid reasons for rejection were adduced because sources of systematic error could be shown to be either definitely present or highly probably for good and sufficient physical reasons. The final set of linearized equations after this censorship was accomplished had a measure of compatibility, $\chi^2 = 3.25$, the expected value in absence of all systematic error being $\chi^2 = 3$ which is not a statistically significant difference in this case. Three years after the 1955 adjustment was completed an error was discovered in the theoretically calculated value of Karplus and Kroll[24] of μ_e/μ_0, the next to the last datum in the group of fixed constants listed in Table 4. As we pointed out in a recent letter to the *Physical Review*,[25] the change of 14.3 ppm in μ_e/μ_0 modifies the numerical values in the case of three of these equations, the third, the fourth, and the eighth. After effecting this modification the seven linearized observational equations take the form shown in Table 5. These equations of Table 5, then, constitute the starting material from which we shall derive all indirect values of Λ implicit in them. The first equation results of course from *direct* measurements of Λ already discussed and we shall therefore make no use of it.

TABLE 5

THE LINEARIZED OBSERVATIONAL EQUATIONS ON WHICH THE 1955 L. S. ADJUSTMENT WAS BASED AFTER CORRECTION OF THE 14.3 PPM ERROR IN μ_e/μ_0

						Weight	Description of Experimental Source	
		x_4	$=$	0	$= A_1,$	0.11	$\Lambda = 1.002020$	(16)
	$x_3 +$	$3x_4$	$=$	3.5	$= A_2,$	0.07	$N\Lambda^3$ (Birge's average)	(17)
x_1			$=$	2.6	$= A_3,$	4.92	Dayhoff fine structure splitting in deuterium	(18)
$3x_1 -$	x_2		$=$	-3.7	$= A_4,$	0.19	Thomas, Driscoll, and Hipple gyromagnetic ratio of proton	(19)
	$x_2 + x_3$		$=$	11.1	$= A_5,$	0.58	(Iodine) Faraday by electrochemistry	(20)
$-3x_1 + 2x_2 +$	x_3		$=$	14.9	$= A_6,$	0.83	Sommer, Thomas and Hipple (omegatron) mag. moment of proton	(21)
$-x_1 +$	x_2	$-x_4$	$=$	-5.6	$= A_7,$	0.015	Short wavelength limit of continuous X-ray spectrum. Mean of low-voltage values	(22)

The remaining six equations can be combined in nine sets of four equations each and one set of three equations, each of the ten sets being just sufficient to obtain a different just-determinate solution for Λ. Table 6 displays these ten solutions and gives the ten numerical results with their standard deviations. Each solution is labeled with a set of numbers (e.g., 2345) which designate which of the constants in Table 5, A_2 to A_7 inclusive, entered into that solution. The writer believes there are no other just-determinate solutions than these ten. While all these solutions are *different*, it must not be supposed that they are *independent* of each other.

TABLE 6

COMPUTATION OF TEN DIFFERENT JUST-DETERMINATE INDIRECT SOLUTIONS FOR Λ FROM THE DATA OF TABLE 5

(The Corrected value of μ_e/μ_0 along with the γ of T. D. & H. are used)

			Parts in 10^5	σ, Ppm	Λ
(1)	$x_4 = {}^1/_3(A_2 + 3A_3 - A_4 - A_5)$	$=$	0.967	16.05	1.002030 ± 0.000016
(2)	$x_4 = {}^1/_3(A_2 + 3A_3 - 2A_4 - A_6)$	$=$	1.267	20.7	1.002033 ± 0.000021
(3)	$x_4 = 2A_3 - A_4 - A_7$	$=$	14.5	85.	1.002165 ± 0.000085
(4)	$x_4 = {}^1/_3(A_2 + 3A_3 - 2A_5 + A_6)$	$=$	1.33	16.5	1.002033 ± 0.000017
(5)	$x_4 = {}^1/_2(A_2 + A_3 - A_5 + A_7)$	$=$	−5.3	45.5	1.001967 ± 0.000046
(6)	$x_4 = A_2 - A_3 - A_6 + 2A_7$	$=$	−25.2	168.0	1.001768 ± 0.000168
(7)	$x_4 = {}^1/_3(2A_2 + A_4 - 2A_5 + 3A_7)$	$=$	−11.9	86.2	1.001901 ± 0.000086
(8)	$x_4 = {}^1/_3(2A_2 - A_4 - 2A_6 + 3A_7)$	$=$	−11.97	86.0	1.001900 ± 0.000086
(9)	$x_4 = {}^1/_3(2A_2 - A_5 - A_6 + 3A_7)$	$=$	−11.93	85.6	1.001901 ± 0.000086
(10)	$x_4 = 2A_3 - A_5 + A_6 - A_7$	$=$	14.6	112.6	1.002166 ± 0.000113

The numerical values of A_2 to A_7 will be found in Table 5.

Many of the solutions utilize one or more equations in common. It would obviously be impossible to derive more than six independent solutions given only the six independent equations. The reader should be warned that because these ten solutions are not observationally independent of each other it would be decidedly incorrect to try to arrive at the least-squares adjusted indirect value of Λ implied by the last six equations of Table 5 by applying the familiar weighted averaging method permissible for independent data (according to which the weights are made inversely proportional to the squares of the error measures) to the ten results of Table 6. The easiest way on the contrary is to perform a least squares adjustment of the last six equations of Table 5 since these equations have purposely been formulated so as to ensure their observational independence. E. R. Cohen has

devised a beautiful and simple way[26, 27] of finding the least squares adjusted *indirect* value of a quantity implied by an overdetermined set of equations, that is to say the least squares adjusted value implied by the entire set of input equations *except* the one which states the directly measured value. We use this method to obtain the least-squares adjusted indirect value of Λ.

In Figure 3, we show graphically, to very expanded scale, these ten solutions

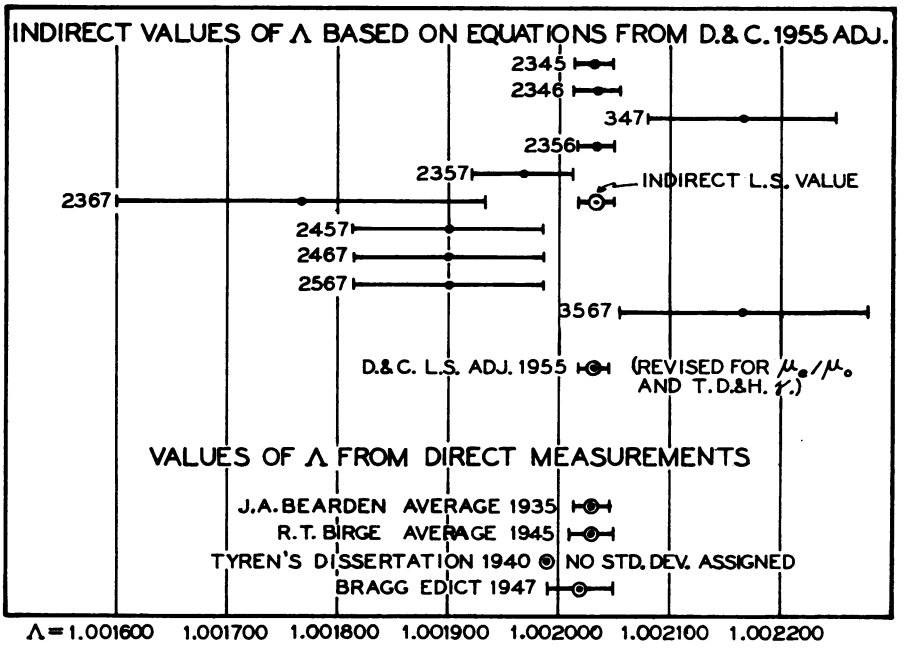

FIG. 3.—Ten different indirect solutions for the conversion constant, Λ, derived from the input data of the 1955 Least-Squares Adjustment of Cohen, Dumond, Layton, and Rollett are here graphically compared with the least-squares adjusted value for Λ of that adjustment and with various directly observed values. In this figure the input data of the adjustment correspond to the data of Table 5, i.e., they have been altered from the original values of 1955 to correct them for the Karplus & Kroll computational error of 14.3 ppm in μ_e/μ_0 discovered in 1958.

and their error measures together with the L. S. adjusted indirect value implied by all of them. In this same figure we also show the least-squares adjusted output value of Λ implied by the entire overdetermined set of equations of Table 5 including the directly measured information. It is worthy of note that the correction of the Karplus and Kroll value of μ_e/μ_0 has brought the L. S. adjusted value of Λ from 1.002039 ± 0.000014 (as given in 1955) down to 1.002031, in better agreement with the Bearden-Birge estimated average value from the direct measurements. We also show in Figure 3, for comparison, Bearden's and Birge's averages of the direct measurement, Tyrén's value (uncorrected for Lamb shift) and the Bragg edict value of 1947.

One of the important contributions to the data of Tables 5 and 6 is the fourth equation of Table 5 based on the well-known measurement in 1950, by Thomas, Driscoll, and Hipple, at the U.S. National Bureau of Standards, of the gyromagnetic ratio of the proton. The experiment was done in the strong field between the iron pole pieces of a powerful electromagnet.

The absolute measurement of the field in gauss was accomplished by weighing the force on a current-carrying wire placed in the magnet gap. The result obtained was, before correction for the diamagnetism of the sample,

$$\gamma_p' = \omega_p/B = (2.67523 \pm 0.00006) \times 10^4 \text{ radians sec}^{-1} \text{ gauss}^{-1} \text{ (T. D. \& H., 1950.)} \quad (23)$$

Now this ratio has been remeasured in 1958 under the U.S. N.B.S. auspices by P. L. Bender and R. L. Driscoll[28] by a different method, this time in a much weaker magnetic field set up by a precision solenoid of very accurately measured dimensions. The proton-containing sample (water) was first polarized in a strong field (about 5,000 gauss) at a distance from the apparatus and shot through a pneumatic tube into the energized solenoid so that its magnetic polarization ended up pointed along the axis of the latter. A short pulse (lasting about 10 milliseconds) of RF magnetic field near the resonant frequency of the protons in the solenoid field, was then applied perpendicular to the solenoid field so as to cause the magnetization of the sample to precess freely for many seconds in the solenoid field and this free precession induced a signal in a pick-up coil, whose frequency after amplification was accurately measured. The result of this measurement yielded a value of the proton gyromagnetic ratio 37.4 ppm lower than Thomas, Driscoll, and Hipple's.

$$\gamma_p' = (2.67513 \pm 0.00002) \times 10^4 \text{ radians gauss}^{-1} \text{ sec}^{-1} \text{ (B. \& D., 1958)} \quad (24)$$

The reason for this discrepancy is not yet clarified.

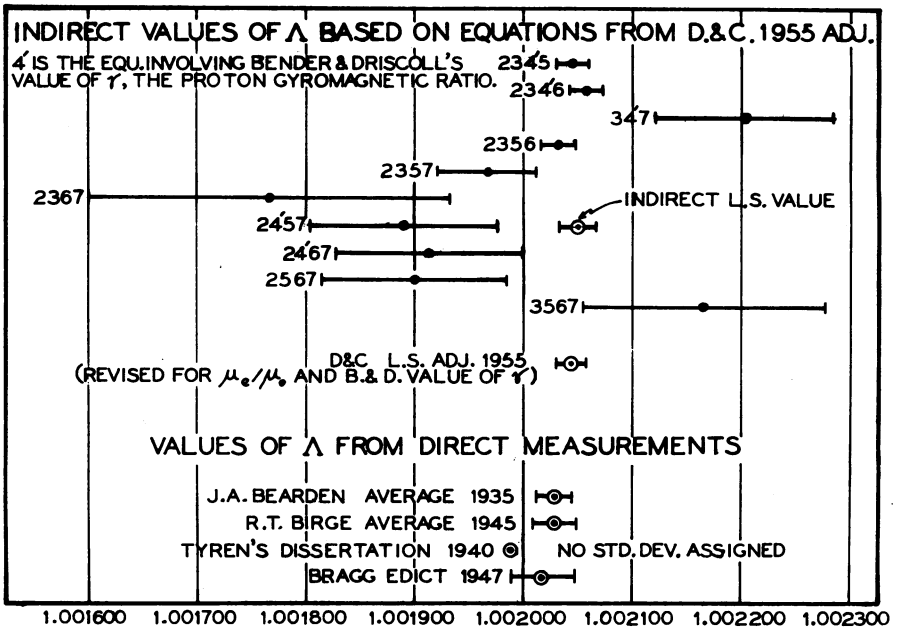

FIG. 4.—The ten different indirect solutions for the conversion constant, Λ, displayed in this figure differ from those in Figure 3 in that the constant, A_4, used in the computations has been changed from $A_4 = -3.7$ to $A_4' = -7.4$. This is the change required if we use Bender & Driscoll 1958 value of γ, the gyromagnetic ratio of the proton, to replace the Thomas, Driscoll, and Hipple 1950 value of that constant occurring in the fourth equation of Table 5.

If now we replace Thomas, Driscoll, and Hipple's γ with Bender and Driscoll's γ, we must change A_4 in the equations of Table 5 from $A_4 = -3.7$ to $A_4' = -7.4$. This will alter five of the solutions for Λ given in Table 6, namely those solutions involving A_4 and designated as 2345, 2346, 347, 2457, and 2467. Table 7 displays these five altered solutions and Figure 4 shows graphically all ten solutions for Λ including those altered by using the Bender and Driscoll datum to replace that of

TABLE 7

RECOMPUTATION OF FIVE OF TEN DIFFERENT JUST-DETERMINATE SOLUTIONS FOR Λ OF TABLE 6 WHICH REQUIRE MODIFICATION IF B. & D. VALUE OF γ REPLACES THE T. D. & H. VALUE

		Parts in 10^6	σ, ppm	Λ
(1)	$x_4 = {}^1/_3(A_2 + 3A_3 - A_4' - A_5)$	2.53	14.4	1.0020453 ± 0.000014
(2)	$x_4 = {}^1/_3(A_2 + 3A_3 - 2A_4' - A_6)$	3.73	14.8	1.0020573 ± 0.000015
(3)	$x_4 = 2A_3 - A_4' - A_7$	18.2	82.3	1.0022020 ± 0.000082
(7)	$x_4 = {}^1/_3(2A_2 + A_4' - 2A_5 + 3A_7)$	−13.1	85.8	1.0018890 ± 0.000086
(8)	$x_4 = {}^1/_3(2A_2 - A_4' - 2A_6 + 3A_7)$	−10.7	85.6	1.0019130 ± 0.000086

The numerical value of $A_4 = -3.7$ has been changed here to $A_4' = -7.4$ parts in 10^6 and its standard deviation has been changed to ±7.66 ppm (B. & D.'s value).

Thomas, Driscoll, and Hipple. The least squares adjusted value of Λ in Figure 4 has also been revised to take into account the change in the input value of γ.

Only three of the ten indirect solutions for Λ displayed either in Figures 3 or 4, namely 2345, 2346, and 2356, are sufficiently accurate to be of interest to us. When we compare the data displayed in the two figures it is clear that the use of the Bender and Driscoll data renders the set somewhat less consistent than does the use of the Thomas, Driscoll, and Hipple datum. It is of considerable interest that the solution, 2356, which does not involve the gyromagnetic ratio determination, A_4, yields a value of Λ which agrees quite well with both the L. S. adjusted value and with Birge's average of the directly measured values, whereas the solutions, 2345 and 2346, for Λ which do depend on A_4, are thrown from good agreement with the L. S. adjusted value and with Birge's average of the directly measured values into disagreement with these when the B. & D. datum replaces the T. D. & H. datum.[‖] Because of the uncertainty at the present moment as to which gyromagnetic ratio determination is the more reliable, the single indirect determination, 2356 acquires considerable importance as the only other source of information on Λ beside the directly measured values. We therefore select it as the one whose experimental bases we shall enumerate in detail to serve as example of the entire set of ten.

DATA OF SOLUTION 2356 FOR Λ

Linearized Form		Primitive Form		
$x_3 + 3x_4 = A_2;$	$N\Lambda^3 = c_2 =$	$Mf/(\rho\phi d_x^3)$		(25)
$x_1 = A_3;$	$\alpha = c_3 =$	$4\Delta E_D^{1/2}[1 + ({}^5/_8)\alpha^2]^{-1/2}[2(\mu_e/\mu_0) - 1]^{-1/2} R_D^{-1}c^{-1}$		(26)
$x_2 + x_3 = A_5;$	$Ne = c_5 =$	cF_I		(27)
$3x_1 + 2x_2 + x_3 = A_6;$	$Ne^2\alpha^{-3} = c_6 =$	$c^2(\mu_e/\mu_0)M_p/(4\pi\mu' KR_\infty)$		(28)

The numerical values associated with these quantities are:

Parts in 10^6	σ (ppm)	σ^2 (ppm)^2	
$A_2 = 3.5$	38.	1440.	$c_2 = 0.606179 \times 10^{24}$ mole^{-1} (Phys.)
$A_3 = 2.6$	4.5	20.2	$c_3 = 0.00729719$ (dimensionless)
$A_5 = 11.1$	13.1	172.	$c_5 = 2.89365 \times 10^{14}$ esu mole^{-1} (Phys.)
$A_6 = 14.9$	11.	121.	$c_6 = 3.57659 \times 10^{11}$ (esu)^2 mole^{-1} (Phys.)

Explanatory notes to above equations follow.

(25) The experimentally measured quantities in the right-hand member of this equation are the molecular weight, M, of a crystal; its macroscopic density, ρ; the geometric factor, ϕ, which differs from unity for rhombohedral crystals such as calcite as explained earlier in this paper; and the interplanar spacing, d_x, measured by means of X-rays and expressed therefore in X-units. All these quantities share in contributing to the error of the result. They appear in none of the other equations, however. f is a pure number, the number of molecules of molecular weight, M, per unit cell. The average value of $N\Lambda^3$ computed by Birge[29] from five different crystals was used.

(26) In this equation the experimentally measured quantities in the right-hand member are ΔE_D, the fine structure splitting in deuterium as measured by Dayhoff, Triebwasser, and Lamb;[30] the Rydberg constant for deuterium, R_D; the velocity of light, c; and the fine structure constant, $\alpha = 2\pi e^2/(hc)$. (It is permissible to use a less accurately known value of α as an input datum here because the bracket, $[1 + {}^5/_8)\alpha^2]^{-1/2}$, is very insensitive to small changes in α). For the anomaly ratio, μ_e/μ_0, of the magnetic moment of the electron to the Bohr magneton, the theoretical formula of quantum electrodynamics[31-34]

$$\mu_e/\mu_0 = 1 + \alpha/(2\pi) - 0.328\,\alpha^2/\pi^2 = 1.0011596 \qquad (29)$$

has been used. (The numerical value results from taking $\alpha^{-1} = 137.039$.) The only substantial contributor to the error in formula (26) is ΔE_D.

(27) In this equation the experimentally measured quantities are F_I, the Faraday constant as determined electrochemically by means of the iodine coloumeter and c, the velocity of light. The latter is needed as a conversion factor because, in the left-hand members of the equations, e denotes the electronic charge in absolute electrostatic units. Only the iodine Faraday is used because the equation corresponding to the Faraday by the silver voltameter was one of those rejected under strong suspicion of systematic error as described above. The discussion of this and other points too lengthy for inclusion in this paper together with descriptions of all the experiments here alluded to may be found in a book *Fundamental Constants of Physics*.[35] Only F_I contributes substantially to the error in this equation.

(28) In this equation the experimentally measured quantities in the right-hand member are c, the velocity of light; M_p, the mass of the proton on the "physical scale" of atomic masses; μ', the magnetic moment of the proton expressed in nuclear magnetons, $\mu_n = eh/(4\pi m_p c)$ (here m_p is the absolute mass of the proton), as determined by Sommer, Thomas, and Hipple;[36] $K = (\mu_e/\mu_p) = [M_p/Nm\mu'] \cdot (\mu_e/\mu_0)$ is the measured ratio of the electron magnetic moment, μ_e, to the proton magnetic moment, μ_p, as measured by Koenig, Kusch, and Prodell[37] and R_∞ is the Rydberg constant for infinite mass. Here μ' is the only substantial error contributor, all the other quantities being treated as fixed auxiliary constants including μ_e/μ_0 which as explained under (26) is computed from the theoretical formula.¶

The formula, 2356, written first in its linearized form and then in its primitive form reads:

$$x_4 = (1/3)(A_2 + 3A_3 - 2A_5 + A_6); \qquad (30)$$

$$\Lambda = (c_2 c_3^3 c_6/c_5^2)^{1/3} = [(N\Lambda^3)\alpha^3(Ne^2/\alpha^3)/(Ne)^2]^{1/3} \qquad (31)$$

The last equality in (31) is easily verified.

What we have done in this indirect solution then can be described in words as follows. We use the value of the Sommerfeld fine structure constant, α, as determined by Dayhoff, Triebwasser, and Lamb's measurement[30] on deuterium along with the determination of Ne^2/α^3 (computed from the Sommer, Thomas, and Hipple "omegatron" measurement of the magnetic moment of the proton[36] combined with five other very accurately measured constants as described under (28) to obtain a value of Ne^2. The square of the electrochemically measured Faraday constant gives us a value of N^2e^2. The quotient then of this latter by Ne^2 gives us N, the Avogadro number. The measurements[29] based on the densities, geometry, molecular weights, and grating constants of five different crystals (the latter determined by X-rays on the X-unit or Siegbahn "crystal scale") gives us the product, $N(\lambda_g/\lambda_s)$ and the desired quantity, λ_g/λ_s, is simply the quotient of $N(\lambda_g/\lambda_s)$ by the preceding value of N.

It should be clear then from this and from the discussion of the measured quantities in equations (25)–(28) what a wide variety of precise physical measurements from many branches of physics and physical chemistry are involved in this indirect determination of Λ, a determination whose result nevertheless agrees quite satisfactorily with Birge's average of the direct measurements of Λ. The two approaches are totally independent.

The indirect solution for λ_g/λ_s which we have just described is only one out of ten different indirect solutions permitted by the 1955 data and involving a wide variety of sources drawn from almost every field of physics. The close and intricate linkage between precision X-ray measurements and all the rest of physics is here well illustrated and indeed it is becoming increasingly clear to nuclear physicists,[40] solid state physicists,[41] and even to physicists studying mesons[42] and other strange particles that they cannot do without precise data from the field of X-rays, data expressed in terms whose definitions must be clear, precise, and unambiguously related to the entirety of the physical system of units and measurements if we are to make progress. It is our duty to see that this comes to pass. Adoption of an arbitrarily defined value for λ_g/λ_s unrelated to the rest of physics is therefore not a step in the direction of progress.

Conclusions as to Our Present Knowledge of Λ and Their Implications for Tabulating X-Ray Wavelengths in Milliangstrom Units.—It seems fairly clear from the analysis of the data summarized in Figures 3 and 4 that the value of Λ indicated by our present sources of knowledge must be not far from

$$\Lambda = 1.002031 \pm 0.000014 \text{ ('55—L. S. adjusted value corrected for } \mu_e/\mu_0). \quad (32)$$

This is the least-squares adjusted value implied by all seven equations of 1955, including the direct as well as indirect data and using *Thomas, Driscoll, and Hipple's γ, after those equations, have been corrected for the error discovered in 1948 in the Karplus & Kroll computed value of μ_e/μ_0.* The as-yet unresolved dilemma between the Thomas, Driscoll, and Hipple-γ and the Bender and Driscoll-γ makes it necessary to take into account also the least-squares adjusted value of Λ implied by the seven equations, direct and indirect, of 1955 with the correction for the error in μ_e/μ_0 *and with the Bender and Driscoll γ.*

$$\Lambda = 1.002044 \pm 0.000014 \text{ ('55—L. S. adjusted value corrected for } \mu_e/\mu_0 \text{ with B\&D-}\gamma) \quad (33)$$

The discrepancy between T. D. & H. and B. & D. is as yet unexplained.** Because of this uncertainty we have at the present moment no choice but to take as our present best information on Λ, an equally weighted mean between the two results given in (32) and (33) which, fortunately, do not differ significantly compared to their standard deviations. It would be quite incorrect to compute the error measure in this mean, however, as though the two results (32) and (33) were independent since they are in fact strongly correlated. The writer suggests the value

$$\Lambda = 1.002037 \pm 0.000020 \text{ (DuMond's best guess, 1959)} \quad (34)$$

The error measure, it will be noted, has been expanded a little "for safety," to cover "possible but unknown" systematic errors. (This sort of guesswork is a prevalent custom which the writer deplores, *especially when it is done without disclosure.* In the present case the reader is at least warned.)

It is fairly evident then that we cannot at present regard Λ as known with a standard deviation much smaller than 20 parts per million. Whether the efforts now in progress to improve upon this precision will effect an improvement of a whole order of magnitude seems doubtful at the present time. For example, the grazing angle of diffraction of the silver $L\alpha_1$ X-ray line diffracted from a grating of 600 lines per mm under a grazing incidence angle of say 10 minutes is 1.29 degrees in the first order and 3.14 degrees in the 6th order. Because the wavelength, λ, is about proportional to the square of the angle of diffraction, in order to measure λ to ± 20 ppm the angle must be measured to ± 10 ppm. Hence in the more favorable of the two above cases (the case of the 6th order) the diffraction angle must be measured to ± 0.11 seconds of arc to match the precision with which we now believe we know Λ. To improve on this precision by a whole order of magnitude, much as we would like to do it, promises to present serious difficulties, whether we hope to do it either by the method of comparison with hydrogenic spark lines or by absolute angle measurements.

Now let us turn to the accuracy with which X-ray wavelengths can be measured on the crystal scale. In the most recent wavelength tables given by A. E. Sandström in the *Handbuch der Physik* these are frequently quoted to six and in many cases to seven significant figures. Over 70 reference lines are there tabulated in X-units out to the third decimal place of that unit. From the writer's own experience with the two-crystal spectrometer this precision is perhaps about the limit of what can be done by very careful replicated work with a precision instrument capable of measuring angles to a small fraction of a second of arc, say 0.1 second or smaller. Taking as a typical case the wavelengths of the $MoK\alpha_1$ line this precision corresponds to about 1.3 parts per million. It should be clear then that a sacrifice of at least a factor of ten or twenty in precision will be the price paid for expressing all these lines on a scale of milliangstroms.

Desirability of Redefining the X-Unit in Terms of One or More Standard X-Ray Emission Lines.—At present most textbooks refer to the "crystal scale" of x-ray wavelengths and define the "X-unit" as a unit such that the "effective" value in first order reflection of the grating constant of the cleavage planes of "purest" or "perfect" calcite at 18°C is

$$d_{18}'' = 3029.040 \text{ X-units.} \quad (35)$$

Different samples of calcite from different parts of the world have been shown by J. A. Bearden[38] to reflect one and the same X-ray line at slightly different Bragg angles ranging over a variation in the first order of some 0.3 second of arc to 0.7 second of arc in the fourth order. Similar small variations have been observed by K. Lonsdale for apparently perfect specimens of diamond. But how then does one know when he is using a sample of "purest" or "perfect" calcite? The answer is that in practice one standardizes one's crystal by measuring a standard oft-measured X-ray line with it such, for example, as the MoKα_1 line. Our practice of defining the unit with which X-ray wavelengths can be most precisely measured in terms of a crystal grating space is simply a vestige of the historical fact that at the outset first Sir William Bragg, then A. H. Compton, and finally Manne Siegbahn based their computation of these wavelengths upon the density, geometry, and molecular weight of a calcite crystal. If, however, calcite were strictly adopted as the conventional standard to define the X-unit it would thenceforth be strictly necessary for the International Bureau of Weights and Measures at Sévres to keep in a desiccator, under extremely carefully controlled conditions, one standard calcite crystal, or perhaps a pair of them for use in a two-crystal spectrometer, against which all other crystals for use by X-ray spectroscopists could be compared. Such a cumbersome procedure is clearly not in the spirit of modern physics where every effort is made to relate our standards to the most fundamentally reproducible natural units or constants obtainable. Just as the meter is, for the most accurate purposes, defined in terms of the wavelength of a spectral line in the optical region, so the x-unit also should be defined in terms of one or more X-ray lines, simply because this is the most reproducible and accurate way to define it. We do not imply by this proposal a *shift in the value of the x-unit*, merely a *sharpening* in the precision of its definition. For this purpose we must select a standard X-ray line or lines whose wavelengths can readily and precisely be compared, by crystal diffraction or other methods, with the wavelengths of most of the several thousand other known X-ray lines (using single or successive multiple steps of comparison with one or more different crystals as tools). Perhaps even some appropriately weighted average of a multiplicity of standard lines, whose wavelengths relative to each other have been determined with exceeding care should be adopted (see an appendix to this paper) as a sort of *collective standard.* In all such work the various crystal grating constants are to be regarded as merely the tools of comparison but the lines are the fixed points in the scale. At the present moment a proposal is extant, with the signatures of Manne Siegbahn and other X-ray people, to define the X-unit at a specific numerical value in terms of the wavelength of the MoKα_1 line. The writer is strongly in favor of adoption of such an improvement in the sharpness of what is meant by the term x-unit, since it would be a distinct step in the direction we should go. The writer does not urge the particular choice of MoKα_1 as a point of great importance. Another choice such as CuKα_1 might turn out to be better and more convenient or again a collective unit based on a weighted average of a multiplicity of very carefully measured standard lines might be even more to be preferred. The important point emphasized here is the adoption of emission lines as the fixed points to define the scale in preference to crystals.

What Feature of an X-Ray Line Profile Shall Be Taken as "The" Wavelength?—The two-crystal spectrometer affords a spectral resolving power amply sufficient

to reveal the "natural structure" of the spectral profile of an x-ray emission line with considerable fidelity. For example, in the case of first order reflection of the tungsten $K\alpha_1$ line from the (310) planes of quartz, the planes lying normal to a 1-mm. thick slab of crystal with the beam transmitted through the slab, a parallel position rocking curve of half width at half maximum height of about 1.4 seconds of arc was obtained (an index of the order of angular and spectral resolving power of the crystals) and this is to be compared with a half width at half maximum height of 14 seconds for the natural line profile,[39] obtained with the same crystals. Unfortunately there is no unanimity of convention as to what feature of the spectral profile of an X-ray line to take as "the" wavelength. The maximum point, the center of gravity or "centroid," the point of intersection of the tangents to the two points of inflexion of the profile, the mean position of the median points of horizontal chords (after subtraction of the background) and the limit of the locus of such median points extended to the peak of the line, have all been used or proposed. In the case of nearly all the X-ray lines determined with photographic spectrometers, a cross hair in the microscope of a comparator is simply made, by a subjective judgment, to divide the blackened image as nearly in its middle as can be estimated. We believe that this latter process comes nearer to determining the median point of horizontal chords near the peak of the profile than to any of the other procedures.

When the natural line profile is distorted (as it must necessarily always be to some extent) by various instrumental causes and other experimental impurities it is sometimes necessary to resort to various "folding" and "unfolding" procedures to reduce one's data. Now there is a beautiful and simple additive theorem relating the centroid of the fold of two profiles into each other to the centroids of the two individual profiles which makes the adoption of the centroid as the fiducial feature of a line profile very attractive and convenient.

Unfortunately there is a real difficulty with adopting the centroid of the profile as the fiducial feature in the case of X-ray lines. It is well known that the "witch" or Cauchy distribution,

$$I(\lambda) = I_{\max} [1 + (\lambda - \lambda_0)^2/W^2]^{-1} \tag{36}$$

sometimes also called a "Lorentzian," describes to quite a good approximation the natural spectral profile of many X-ray lines and in particular does so rather well out to several half widths, W, as regards the law of decay of the "tails" of the line, a law which at great distances is like the inverse square of the distance from the peak. In a strict mathematical sense the witch profile has no centroid since its first moment diverges logarithmically. It is, of course, an easy matter to redefine what we mean by "the centroid," provided the profile is strictly a Cauchy distribution, or indeed simply provided the profile possesses an intrinsic axis of symmetry, so as to establish the center of symmetry in a definite way. But to do this we must always "beg the question" a little by making appeal to some other feature of the profile beside the centroid in order, by successive approximations to ensure that the limits over which we extend our integral in determining the centroid, shall be sufficiently symmetrically located relative to the peak. But if the profile has no intrinsic axis of symmetry, i.e., if the curve is not an even function but a sum of an even and an odd function, then the slow decay of the tails of the lines can introduce

a considerable shift in the position of the centroid and indeed one cannot be strictly sure about this position without exploring the tails of the curve out to very great and unfortunately quite indeterminate distances from the peak. Now the unfortunate truth is that most X-ray lines when studied with great care are not strictly Cauchy-like in shape and worst of all *do not have an axis of symmetry* but they do exhibit the slow law of decay (approximately inverse square) in the tails which is the root of all this trouble since it renders the position of the centroid objectionably sensitive to small vagaries and asymmetries of profile at large distances. In practice we do not know where to chop off the tails of the line in choosing the beginning and ending points of our integration to determine the centroid. If we truncate the tails too much and the line has a small unsuspected asymmetry extending far into the tails we may be incorrectly biasing the centroid position by our arbitrary choice of the truncation points. If, on the other hand, we extend our integration limits too widely we shall be introducing unnecessary uncertainty into the centroid position because of the random statistical fluctuations in the tails, an uncertainty which increases as the square root of the distance we extend the limits. For these reasons the centroid position is perhaps the poorest feature of an X-ray line profile from the point of view of definiteness and reproducibility.

There is a still more important consideration in this connection, however (than the uncertainties attending the determination of the centroid), as a warning against its indiscriminate or incautious use. This is the fact that the present tabulated X-ray wavelengths *do not refer to the centroids of the corresponding line profiles.* The great majority of these wavelengths have been photographically determined by placing the cross hair of a comparator microscope subjectively on the center of a streak of photographic blackening and they refer to something that may be described roughly as the peak and which this writer believes is probably best found by the procedure above referred to as the limit of the locus of the centers of chords extended upward to the peak of the profile. It is possible that, with a great deal of careful labor exploring profiles with the two-crystal spectrometer out to many half-widths, the shift of the centroid of any specified line profile away from the peak position (as defined above) could be determined. Frequently quite closely adjacent lines in the spectrum have different asymmetries so that the relationship between centroid and peak is today an unknown quantity which would have to be determined for a very great number of lines. It is therefore problematical whether the mathematical simplification gained by use of the centroid will make this worth the effort in view of the real experimental difficulties in fixing the centroid by reason of the extended asymmetries and statistical fluctuations in the tails aforementioned.

SUMMARY

The system of some 3,000 X-ray emission line wavelengths, some of which have been (and many more of which can be) measured *relative to each other* to a precision approaching a very few parts per million by refined crystal diffraction methods, constitutes an extremely reliable and valuable set of fixed points in our scale of length magnitudes in the general region of atomic dimensions. Manne Siegbahn, circa 1930, utilizing the best values then available of N, the Avogadro number, combined with the density of calcite, the geometry of its lattice and the atomic weights of its constituents, computed a value for the grating spacing of the

cleavage planes of calcite. After taking into account the effect of the refractive index of X-rays in calcite this led to a value for the "effective" grating constant for first order Bragg reflection from the cleavage planes of 3,029.040 milliangstroms. This value was incorrect because the value of N which he had used in its computation was erroneous, but Siegbahn, who had no way of knowing this, used this erroneous result to establish a measuring unit for X-ray wavelengths which he intended to be 1 milliangstrom (10^{-11} cm) but which he very wisely called by a distinctive name "the x-unit" probably because, even at that time, he felt less security regarding his knowledge of its relation to our macroscopic standards than he could wish in view of the excellent reproducibility of the X-ray wavelength measurements relative to each other. For this purpose Siegbahn had taken a value of N computed as the quotient of the Faraday by Millikans "oil drop" value of the electronic charge. This last has later been shown to be too small by nearly 0.6 per cent. More precise later direct measurements of X-ray wavelengths using artificial ruled gratings have shown that the total effect of all the systematic errors in the constants Siegbahn adopted made his X-unit a little over twenty parts in ten thousand larger than one milliangstrom. Since the chief uncertainty regarding the absolute value of X-ray wavelengths concerns only the value of a single conversion factor, $\Lambda = \lambda_g/\lambda_s$, i.e., the ratio of a given wavelength expressed in milliangstroms, λ_g (on the "grating scale"), to the same wavelength expressed in X-units, λ_s (on the Siegbahn or "crystal" scale), it has become customary, in quoting X-ray wavelengths to high precision, to express them on Siegbahn's nominal scale of X-units defined in terms of the calcite grating space. Calcite, however, has been shown to be less reproducible from sample to sample than are the wavelengths of appropriately selected X-ray lines so that for purposes of maximum precision and reproducibility, this author believes it would be still better to define the X-unit (or some arbitrary unit for measuring X-ray wavelengths) in terms of one or more carefully selected X-ray emission line wavelengths.

This paper surveys all our present sources of both direct and indirect information on the conversion constant, Λ, and examines their probable reliability. Such a survey is of current interest because of a proposal now seriously being discussed among X-ray crystallographers to express all the standard X-ray emission line wavelengths, whose values are to be published in the new International Tables of Crystallography, in angstrom units. It is alleged that this step should be taken in the interest of simplification and to avoid errors and misunderstandings. This paper aims to show that unless the precision of our present knowledge of Λ can be improved by at least an order of magnitude, the above proposal will require either (1) seriously downgrading the precision with which all the emission line wavelengths are quoted (in angstrom units) for the use of crystallographers or (2) adopting some *conventionally defined value* of the conversion constant, Λ. In the latter case the numerical values of the X-ray wavelengths arrived at by its use will be neither fish nor fowl for they will be expressed neither in x-units nor truly in angstrom units but in a third new conventional unit which, unless it be given a distinguishing name, will lead to even more confusion than at present. Emphasis is placed on the fact, frequently overlooked by specialists in a given discipline, that the entire system of measurements of Physics and Chemistry has become so closely and quantitatively interrelated (an interrelationship which becomes ever tighter and more intricate

with time), that we cannot arbitrarily tamper with one part of the system without affecting all the rest. The temptation to dry to circumvent a metrologically difficult determination of a badly needed conversion factor by adopting a conventional definition for it worsens the situation by introducing overdetermination, inconsistency, and semantic confusion. Ten different "indirect" solutions for Λ, computed by appropriately combining different precise measurements of combinations of the atomic constants (other than the direct determination of X-ray wavelengths by means of gratings) are given. Two least-squares adjusted indirect values implied by all this information area:

$$\Lambda'_{(\text{Indirect})} = 1.002034 \pm 0.000016 \text{ (using T. D. \& H value of gamma)}$$

$$\Lambda''_{(\text{Indirect})} = 1.002051 \pm 0.000016 \text{ (using B. \& D. value of gamma)}$$

depending, respectively, on whether the value of gamma, the proton gyromagnetic ratio as measured by Thomas, Driscoll, and Hipple, or that of Bender and Driscoll is used. (In these indirect calculations only the iodine value of the Faraday has been used. See footnote below with symbol[‖]).

These values are to be compared with the average of directly measured values of Λ of Birge (and also earlier of J. A. Bearden) namely

$$\Lambda_{(\text{Direct})} = 1.002030 \pm 0.000020 \text{ (Birge, Bearden).}$$

The direct and indirect values depend on completely independent sources of data Since the discrepancy between these two values of gamma (T. D. & H. or B. & D) remains so far unexplained we have no choice for the moment but to compute Λ under both hypotheses and take the average. The least-squares adjusted best value from both indirect and direct sources of information taking an equally weighted average between the results obtained when the two different values of gamma are used, yields

$$\Lambda = 1.002037 \pm 0.000020 \text{ (DuMond's best guess, 1959).}$$

The error estimate here has been slightly increased above the calculated standard deviation (± 0.000014) to allow for the possibility of systematic errors.

Summary of Conclusions.—It is the present opinion of the writer that:

1. The conversion constant, $\Lambda = \lambda_g/\lambda_s$, is not at present known with sufficient precision to permit tabulating the standard x-ray emission line wavelengths in milliangstrom units without a serious sacrifice of the precision with which these wavelengths are now known relative to each other. Since X-rays are an important part of the general structure of Physics it is undesirable to adopt a conventional value for Λ which may later turn out to be inconsistent with the remainder of that discipline.

2. The unit in which X-ray wavelengths, using crystal diffraction methods, can be measured with highest accuracy should be redefined by tying it to one or more standard X-ray emission lines and abandoning its present conventional definition in terms of "purest" or "perfect" calcite.

3. Great care and circumspection should be used in defining the fiducial reference point on the natural profile of an X-ray line which shall be taken as "the wavelength." The tabulated wavelengths at present in general usually correspond most nearly to the peak because of the methods used in their determination.

The centroid of the profile does not necessarily coincide with the peak by any means and while it possesses certain attractive mathematical properties the difficulties of establishing its relationship to the tabulated peak values in a reliable way are considerable and as yet not in most cases surmounted.

APPENDIX

A Tentatively Suggested Method of Defining a Collective X-Ray Standard of Wavelength Based on a Multiplicity of Selected and Very Carefully Measured Emission Lines.—The suggestion in the body of this paper that a precision unit for measuring X-ray wavelengths could be defined in terms of a multiplicity of selected standard emission lines, perhaps requires a little amplification to make the contemplated procedure clear. It has been pointed out in correspondence by M. Siegbahn, Y. Cauchois, and others that probably no single reference line can be chosen which will serve equally well as a standard for work in all regions of the extensive X-ray spectrum. The spectral gamut of γ-rays and X-rays which has been studied by crystal diffraction is so huge (extending from 6.2 X-units wavelength in the case of some of the studies of neutron-capture gamma radiation from titanium by J. W. Knowles at Chalk River, Canada, to 10,000 X-units in the case of very soft X-rays) that crystals of different kinds and with different interplanar spacings are naturally chosen as most suitable for studies in different regions. This does not, of course, preclude setting up a reliable precision scale over the entire gamut because there is a wide variety of good crystals from which to choose and each crystal is suitable for work over such a wide spectral range that these different ranges overlap very generously and afford ample opportunity to measure numerous X-ray lines in common when the different interplanar spacings of different crystals are being precisely intercompared. It would, however, be clearly much more convenient to have a multiplicity of reference points in the X-ray wavelength scale distributed in such a way that one or more of them would be readily and conveniently available for standardizing almost any crystal or any general spectral domain with which an investigation might be concerned. Naturally this entire system of standard reference lines should have had the wavelengths of its members all measured and intercompared with extreme care, and by different laboratories, using as many varieties of crystal as needed to obtain best results. When sufficiently satisfactory agreement as to the relative wavelengths of these reference lines would be reached it should be possible, in terms of the statistical uncertainties of the mean values of each of the measured standard wavelengths, to attach weights (inversely proportional to the squares of said uncertainties) to each reference line wavelength. Then the X-unit (if that name may still be retained) would be defined by giving the following procedure for determining to high precision the "effective" d in X-units for any reflection in any crystal one might be planning to use. One would measure, with the crystal to be normalized or standardized, the "effective" d as indicated by the Bragg angles observed with as many of the standard reference lines as were conveniently accessible with that crystal. Because of small errors of measurement each reference line would yield a slightly different d for the crystal planes in question. The weighted average of all these d's, using the standard weights already established for the different reference lines, would then be taken as the d of that set of crystal planes in that crystal. This procedure has the advantage that it would permit

the worker standardizing his crystal to choose, from a wide range of possibilities, any degree of precision he might desire consistent with his requirements. To standardize a given set of crystal planes with the highest possible precision he would measure the largest possible number of reference lines accessible to that crystal which his facilities would permit. The weighted average of the d-values obtained with all of these lines would then give the crystal's d as accurately as it could be ascertained. Its accuracy could furthermore be reliably estimated by the familiar methods of computing the precision measure of the mean of weighted observations. On the other hand a standardization of this crystal in terms of one single most convenient reference line might yield sufficient accuracy for the purposes contemplated, in which case the other reference lines would be ignored. Thus the d of a crystal standardized in terms of nine reference lines whose wavelengths might have been preestablished say with equal precision would be known three times as accurately as one which had been standardized with only one of the lines. The collective X-unit defined in this way by the entire array of reference lines would be more accurately fixed than it could be defined in terms of any single line.

Since X-rays comprise a very important range of the physical quantum energy spectrum, and since this is intricately and inextricably involved with all the rest of the measurements made by physicists in every branch of their all-important discipline, the duty devolves upon us to see that the highest possible precision is established here. In the long run nothing save the very best that can be done will be good enough.

* Work supported by the Atomic Energy Commission, the Office of Ordnance Research, and the National Science Foundation.

† These values are not the present international atomic weights but rather essentially the values used by Bragg in 1914 (with slight modification by Siegbahn[1] to obtain an accuracy of one additional significant figure). The present weight for rock salt is 58.454.

‡ Stenström in 1919 demonstrated the existence of a slight deviation from Bragg's law, $n\lambda = 2d \sin \theta$, which he correctly attributed to the fact that X-rays have an index of refraction in the material of the crystal slightly lower than unity. In order to satisfy Bragg's law connecting λ and θ, slightly different "effective" values of the grating constant, d, depending on the order number, n, must replace the true d. For high orders d-effective approaches the true d. In the case of Bragg reflection in the nth order from the calcite cleavage planes, an empirical formula for the effective grating constant d_n, is $d_n = [1 - 135 \times 10^{-6}/n^2]d$ where d is the true grating constant of those planes. This correction, however, only applies in this form to "Bragg reflection" where the X-rays enter and leave the crystal through the same boundary surface and the reflection is from planes parallel to that surface. For internal reflection in a slab of crystal from planes normal to the two (parallel) exit and entry surfaces the correction vanishes.

§ R. T. Birge has assured the writer that he had no part in deciding the manner in which this value was recommended to the public, a manner very foreign to Birge's own meticulous and detailed disclosures of his sources of information and bases for arriving at values.

‖ The writer is indebted to P. L. Bender who read the manuscript for pointing out the following remark in a private communication received after this manuscript had been submitted for publication. Quoting Bender directly: "In your evaluation of the X-ray conversion constant with our recent value for the proton gyromagnetic ratio, you have used only the iodine value for the chemical Faraday. While this experiment is perhaps less suspectible to systematic errors than the silver Faraday, I don't believe that you would have excluded the silver value completely in 1955 except for its conflict with the physical Faraday determined from the gyromagnetic ratio and omegatron experiments. The conflict, of course, came out in your treatment as a large value for chi-squared when the silver value is included. However, as we have pointed out previously, if our recent gyromagnetic ratio value is used with the omegatron result the physical Faraday is

about half-way between the iodine and silver values. It thus seems that for consistency one would have to include both values with some form of weighting. Clearly, a wide difference of opinion can occur as to what weightings should be used for the Faraday values and the gyromagnetic ratio results. This range of opinion seems to me to be the actual limit on our knowledge of the constants at present rather than the statistical errors quoted for the individual results going into the least squares adjustment." (End of quote.)

There is no doubt that had the silver Faraday been included among the data and given weight comparable to the iodine Faraday, the data using Bender's value of gamma would have appeared more consistent. However, the present writer's misgivings regarding the correctness of the silver Faraday are of much longer standing than the conflict with the "physical Faraday" referred to in the above quotation. They date in fact all the way back to 1940 when the writer noticed that the apparent difference between the two sets of values of e/m which R. T. Birge once distinguished as "spectroscopic" and "deflection" values could be largely wiped out by using the iodine Faraday to deduce the "spectroscopic" values in place of the silver Faraday. It then occurred to the writer that the fact that iodine is monoisotopic whereas silver occurs naturally in two isotopes of nearly equal abundance might be significant and he has been agitating ever since for a reinvestigation of this whole question in the light of our modern knowledge of isotopes. All the early precision determinations of the Faraday, circa 1900–1910, were made before the existence of isotopes and their selective participation in electrolysis was known. The question of the reliability of the silver Faraday is still an open one.

¶ It will be noted that each equation involves only one experimental factor which contributes significantly to the numerical error or uncertainty and a *different one* for each equation, all the other data in the equation being so much more accurately known as to contribute essentially not at all to the error. Care has been taken purposely to formulate the observational equations of the least-squares adjustment in this way for unless this is done, i.e., if two or more equations have an essential error contributing factor in common, the equations are not statistically independent, in which case the simple classical weighting procedure for finding the least-squares solution is incorrect. If two or more of the observational equations have an essential error contributing factor in common, it is in fact no longer possible to assign independent weights to the equations, but a weight matrix for the complete set must be used and the computation is considerably complicated thereby.

** McNish at the U. S. National Bureau of Standards has suggested that perhaps the discrepancy in the γ-results of T. D. & H. and B. & D. could be explained by the possible existence of a slight misalignment of the centers of the two circular iron pole faces of the T. D. & H. electromagnet. Apparently these faces were carefully checked for parallelism but not for centering on the same axis. Such a displacement could occasion a slight obliquity of the magnetic field from the normal to the faces (the direction it was assumed to have had) and this in turn would introduce a cosine error into the absolute measurement of the field intensity by the force on the current-carrying conductor. The proton resonance frequency, on the other hand, always corresponds to the absolute value of the field intensity independent of its direction. Unfortunately the magnet having been dismantled, it is now impossible to verify whether such a hypothetical misalignment of the poles actually existed in sufficient amount to explain the discrepancy. Unsuspected nonlinear effects in the relation between ω_p and B might also be present in either of the two experiments.

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[42] The study of the X-rays emitted when either π^- or μ^- mesons replace electrons in atoms has become a very fruitful tool for determining masses and other properties of mesons and also for exploring the region close to the nuclear periphery and even inside it. The characteristic X-ray lines emitted from mesonic atoms have been studied by the use of absorbers and an accurate knowledge of the X-ray absorption edge profiles of these latter has in consequence taken on considerable interest and importance. Only a very small fraction of such work can be cited here. Koslov, Fitch, and Rainwater, *Phys. Rev.*, **95**, 291 (1954); Cohen, E. R., K. M. Crowe, and J. W. M. DuMond, *Phys. Rev.*, **104**, 266 (1956); Garwin, R. L., D. P. Hutchinson, S. Penman, and

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*LASTING AFTER-EFFECTS PRODUCED IN RATS BY SEVERAL COMMONLY USED DRUGS AND HORMONES**

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Communicated May 4, 1959

This is an era of the widespread use of drugs and hormones in the treatment of a great variety of illnesses. New medications appear on the market almost every day; as a matter of fact, many of the members of this audience undoubtedly have been treated with one or more of these new therapeutic agents.

Although the use of many of these drugs has resulted in great gains in the treatment of various ailments, these highly desirable results have often been accompanied by the development during treatment of a variety of undesirable side-effects. In many instances these accompanying effects have been sufficiently serious to necessitate discontinuation of the medication. It is on this account that new drugs and hormones have for some time been screened using animals not only for possible immediate toxic effects but also for any side-effects that might develop during prolonged treatment.

The possibility that in addition to such concomitant side-effects the administration of some of the commonly used drugs and hormones may be followed by serious and permanent pathological after-effects has not received much, if any, attention.

I bring this up because we have noted in experiments made on rats for quite different purposes[1] that the prolonged administration of a number of commonly used therapeutic drugs and hormones has resulted in pathological effects that only appeared well after the end of the treatment; characteristically, once developed, these persisted throughout the remaining life of the animal. Though these effects revealed themselves both in behavior and in metabolism they were not obvious on ordinary inspection. Thus, the rats appeared to be quite normal—in particular, they were free of all the common signs of deficiency such as loss of hair, motor disturbances and nervousness. That despite this they actually were quite abnormal could only be detected through scrutiny of daily records, taken over long periods of time, of their spontaneous running activity in revolving drums, their food and water intake, and the functioning of their reproductive tracts.

Before presenting some records typical of these animals, a short description should be given of the conditions under which the observations were made. The rats were kept separately in activity cages consisting of a revolving drum, a cyclometer, and a small living compartment with a nonspillable food cup and a 100-ml graduated inverted water bottle.[2] Records were made daily of running activity, food and water intake, as well as of the vaginal smears. The external conditions, room temperature, etc., were kept as nearly constant as possible, and were free from any regularly recurring disturbances or variations.